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A STUDY OF THE REACTION BETWEEN MERCURIC CHLORIDE AND AMMONIUM OXALATE

A Dissertation

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

1927

BY

THOMAS HUGER HAZLEHURST, JR.

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ACKNOWLEDGMENT

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I. INTRODUCTION

The reaction between mercuric chloride and oxalates has often been investigated but only in a qualitative or semi-quantitative way. It has been supposed to follow the simple equation,

$$2HgCl_2 + (NH_4)_2\,C_2O_4 = Hg_2Cl_2 + 2CO_2 + 2NH_4Cl$$

The course of the reaction has always been followed by the production of calomel.

The chief characteristics of the reaction may be summarized briefly as follows. In the dark the reaction proceeds very slowly if at all, even at temperatures approaching the boiling point. In the presence of radiation the formation of calomel is qualitatively proportional to the intensity of the light, being quite rapid in direct sunlight and much slower in diffuse light. Eder in his Handbuch der Photographie [1] advocates the use of the photosensitive mixture to give a measure of the amount of ultra-violet radiation in sunlight. The speed of reaction is slow in acid media, one investigator actually claiming that no reaction takes place between oxalic acid and bi-chloride of mercury until enough caustic soda has been added to neutralize the acidity of the mixture.[2] This, however, is not true.

Probably the feature of the reaction most interesting to the early investigators was that this is an induced reaction. Many substances will promote the speed of the reaction, and a few, of which potassium permanganate is the most important, will cause the reaction to proceed in the absence of light.[3] Much work has been done in the endeavor to show that this reaction proceeds when it is coupled with another oxidation-reduction reaction.[4]

Another most interesting feature of the reaction is the fact that the production of calomel is markedly diminished by the presence of oxygen. Under an atmosphere of this gas considerable time must be allowed, even in direct sunlight, for a weighable precipitate of calomel to form. Hydrogen, nitrogen, and carbon dioxide are alike in that they all allow the formation of calomel to proceed rapidly.[5]

PURPOSE OF THE INVESTIGATION

The original motive of the investigation was interest in the induction of the reaction by manganese and other inductors. It was thought that the inductor might, by taking part in the reaction or in some other way, influence the course of it. That is, it was considered possible that the stoichiometry of the process when induced might very well differ from that when it went on of itself. When, as appeared in the course of the investigation, it proved that even the "simple" reaction was most complex, our attention was turned to it and in consequence this whole work has been devoted to a study of the simple reaction with a view to establishing a firm foundation for future study.

EXPERIMENTAL

Our first endeavor was to establish the stoichiometry of the reaction. To this end it was attempted to measure the ratio of carbon dioxide produced to calomel produced. The analysis is fraught with difficulty, since it was early discovered that the gas could not be boiled out of the solution. It was found that boiling, particularly in the presence of excess oxalate, greatly accelerated the production of metallic mercury, the presence of which was readily detected by the darkening of the precipitate of calomel. Furthermore, calomel is volatile to an appreciable extent even at 105°, a fact which made drying the substance in an oven before weighing a somewhat risky procedure.[5] The first workable scheme was as follows:

The reacting mixture was placed in a large Erlenmeyer flask so that the liquid formed a broad and relatively shallow layer on the bottom of the vessel. This secured a quite uniform illumination of the whole mass. The appropriate gas was bubbled through the liquid and served not only to provide the requisite atmosphere, but also to agitate the mixture to some extent and thus to aid in obtaining uniform action. When the reaction had proceeded far enough, concentrated hydrochloric acid was added in sufficient quantity (10% by volume) to prohibit calomel formation, and, as a further precaution, the flasks were protected from direct radiation by means of a screen. The current of gas was then arrested and the solution put under a partial vacuum by means of an ordinary water pump. Under this pressure the solution boiled at about 55°, and the speed of formation of metallic mercury was sufficiently slow to prevent appreciable darkening of the calomel. Even under these circumstances, however, if the boiling were long continued some precipitates were spoiled by metallic mercury.

The issuing gases of the reaction vessel, both during the reaction and the subsequent boiling, were led through a bubbling tube containing concentrated sulfuric acid and then into a tower, the bottom of which was packed with anhydrous calcium chloride previously saturated with carbon dioxide, and the top packed with phosphorus pentoxide. After being thus dried, the gas was passed through a

tared Fleming absorbtion bulb in which the carbon dioxide was absorbed and weighed. The outlet of the Fleming tube was protected from water vapor from the pump by a tower containing calcium chloride and phosphorus pentoxide, the pentoxide being nearer the Fleming bulb. The calomel was then filtered into a weighed Gooch crucible, washed with water and alcohol, and dried for one hour at 105°. The quantity of carbon dioxide was so small and the uncertainty of having extracted and collected all of it was so great that the method was abandoned. No checks could be obtained between ratios measured on different days, and sometimes not even between those obtained on the same day. The general results, as may be seen from the appended figures, showed qualitatively that the ratio $\frac{2CO_2}{Hg_2Cl_2}$ was least in hydrogen and greatest in oxygen, nitrogen occupying an intermediate position nearer hydrogen than oxygen. Cylinder hydrogen was used, freed from all oxygen by being passed over heated platinized asbestos. No precautions were taken to remove traces of oxygen from the nitrogen.

The solutions used in the reaction were Eder's solutions and were made up as follows. The bichloride solution was 50 grams to the litre and the oxalate 40 grams to the litre. 60 c.c. of oxalate were added to 15 c.c. of bichloride. These are not the proportions which Eder used. His were two parts of oxalate to one of bichloride. The materials were C. P. mercuric chloride and C. P. crystalline ammonium oxalate. In the table below and in all the tables which follow r, the quantity we desired to measure, is the ratio of ammonium oxalate consumed to calomel produced, a molal ratio based on the formula Hg_2Cl_2 for calomel. The runs bracketed together and marked simultaneous were run together and for the same length of time. The other columns in Table 1 explain themselves.

TABLE 1

Atmosphere	Grams Hg_2Cl_2	Grams CO_2	Mille equivalents CO_2 / " Hg_2Cl_2 = r	
H_2	0.4879	0.069	0.769	Simultaneous
	0.5192	0.0317	1.000	
	0.7724	0.1332	0.934	
	0.4074	0.0724	0.943	"
	0.6848	0.1268	1.004	
	0.6461	0.1192	1.006	"
	0.6371	0.0943	0.806	
	0.6075	0.0868	0.775	"
O_2	0.0382	0.0177	2.51	
	0.0653	0.0121	1.004	"
	0.0910	0.0227	1.335	
	0.2858	0.0647	1.233	
	0.2220	0.0496	1.206	"
	0.0501	0.0160	1.733	
	0.0385	0.0117	1.650	"
N_2	0.2939	0.0703	1.298	
	0.6934	0.1442	1.129	"
	0.5909	0.1217	1.119	
	0.4456	0.0996	1.214	
	0.4789	0.1037	1.174	"
Air	0.2506	0.0567	1.229	
	0.2119	0.0369	0.943	"

The next method attempted was to extract the carbon dioxide by repeated evacuations with a Toepler pump and either measure the gas volumetrically or absorb it in standard barium hydroxide and titrate with standard acid. The method was tested by adding sulfuric acid to a weighed quantity of pure sodium carbonate and subjecting the solution to several evacuations interspersed with sweeping with air. It was found that ten evacuations and four sweepings extracted only 0.8 of the carbon dioxide known to be there. The method was accordingly discarded.

Finally it was determined to attack the reaction from the other direction. When it had proceeded for some time, the calomel was

filtered off, the filtrate acidified and saturated with hydrogen sulfide to precipitate excess mercury, the sulfide filtered off, that filtrate boiled to remove hydrogen sulfide, and then titrated with standard permanganate after the addition of sulfuric acid. The object of precipitating the excess mercury, besides affording a check on the total quantity of mercury, was to avoid having the reaction proceed farther on the addition of permanganate, which is a strong inductor of the reaction. The original mercuric chloride and ammonium oxalate solutions were standardized, the one by weighing mercuric sulfide and the other against standard permanganate. As the figures below show, the total amount of mercury was accounted for and complete checks obtained between the runs.

TABLE 2

	No. 1	No. 2	Blank No. 1	Blank No. 2
Oxalate added cm^3...	20.00	20.00	20.00	20.00
" left " ..	15.56	15.54	20.04	20.04
" used " ..	4.44	4.46	....	....
" " in mille equiv.	1.601	1.608	10.00 $cm^3 HO_2$ added to	
Mille equiv. Hg put in	1.973	1.973	make up the	
" " Hg_2Cl_2...	1.898	1,903	volume.	
" " Hg S....	0.092	0.089		
Total Hg.....	1.990	1.992		
ratio $\frac{2CO_2}{Hg_2Cl_2}$.....	0.843	0.845		

It will be observed that the total amount of mercury put in was 1.973 mille-equivalents, and that the total of calomel and mercuric sulfide was 1.99 for both runs. Also the blanks show that no oxalate was decomposed during the period of the run in the absence of mercuric chloride.

The method was further tested by adding to a known quantity of oxalate three times the amount of hydrochloric acid equivalent to the chloride in solution. It was found to alter the permanganate titre only slightly:

calc. = 38.67 cc.; obs. = 38.70 c.c. (Error 0.1%).

Also a known amount of oxalate was saturated with hydrogen sulfide

and boiled until the vapors no longer darkened lead acetate paper and then titrated. It is obvious that the hydrogen sulfide does not affect the titration.

calc. = 38.67 c.c.; obs. = 38.66 c.c.

Having now a method of attack of known accuracy, runs were made under different atmospheres and with different ratios of the constituents. The results were most surprising. They are summarized below. It was found impossible to obtain checks on different days for the same solutions or on the same day for different solutions.

In Table 3 the first column tells under an atmosphere of what gas the run was made. Columns two and three show, respectively, the volumes of oxalate and bichloride solutions put into the reaction vessel. Column four contains the values of ρ, the ratio of the two preceding columns. Column six is self-explanatory and column seven shows the values of r, which has been previously defined. The solutions used were 0.4 N in all cases.

TABLE 3

Atmosphere	Oxalate cm³	Bichloride cm³	$\frac{\text{Oxalate}}{\text{Bichloride}} = \rho$	Oxalate consumed mille-equiv.	Ratio r	
	40	10	4	1.600	0.991	Simultaneous
	20	10	2	1.203	0.964	
	10	10	1	0.653	0.861	
	10	20	½	0.329	0.794	
H_2	40	10	4	2.068	1.293	
	20	10	2	2.019	1.071	
	10	10	1	1.744	0.845	"
	5	10	½	1.432	0.899	
	40	10	4	1.330	1.162	
	20	10	2	0.941	1.071	
	10	10	1	0.674	0.901	"
	10	20	½	1.144	0.812	
O_2	40	10	4	0.638	1.201	
	20	10	2	0.395	1.656	
	10	10	1	0.252	0.908	"
	10	20	½	0.387	0.938	
H_2	20	10	2	1.590	0.832	
O_2	20	10	2	1.536	1.913	"
Vacuum	20	10	2	1.572	0.816	

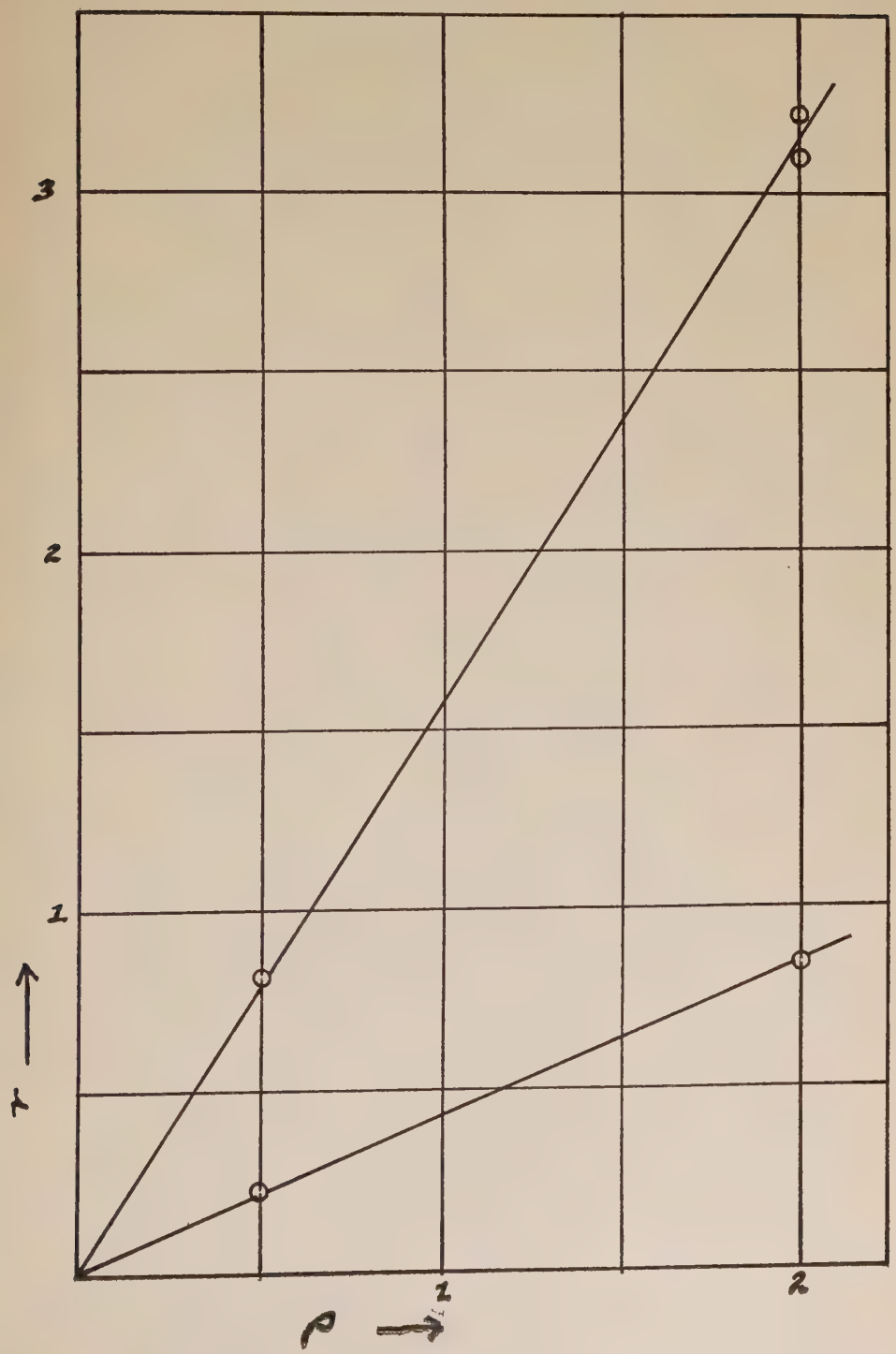
Table 3 shows that there is a distinct trend of the values of r corresponding to those of ρ. Apparently the ratio r varies with the concentration of the components, and the change in this concentration during the reaction was large at all times and in the extreme case, the eighth hydrogen run, the oxalate concentration varied by 75%. The runs are not, then, comparable. In general it may be seen that r is higher for oxygen runs than for hydrogen runs of the same composition.

These runs were all made with only small total volumes (less than 50 cm^3) so that the change in concentration due to the progress of the reaction was relatively great. It was a logical development to use large volumes and to allow the reaction to proceed only a short time. This was done and the results are appended below. The volumes used were either 300 or 225 cm^3.

TABLE 4

Atmosphere	ρ	Oxalate consumed	r	
H_2	2	8.80	0.869	Simultaneous
O_2	2	9.15	3.14	
Vacuum	2	8.70	0.857	
H_2	2	1.356	0.852	"
O_2	2	1.364	3.20	
Vacuum	2	1.355	0.850	
H_2	½	0.684	0.214	"
O_2	½	0.690	0.829	
H_2	½	0.537	0.207	"
H_2	2	1.071	0.836	

The Figures in Table 4 show with probably small error the effect of atmosphere and concentration on the reaction. It will be seen that the values of r for simultaneous runs under hydrogen and in vacuo are identical and are much lower than those under oxygen. Also the quantities of oxalate consumed during the process were about the same for hydrogen, oxygen, and vacuum so that the difference in r is due to a variation in the amount of calomel precipitated. Furthermore, it was observed that changing ρ fourfold has quantitatively altered r fourfold, and that altering the concentration of oxalate twofold causes twice as much oxalate to be consumed. The accompanying graph showing values of ρ plotted against those of r gives an idea of the properties of the reaction.


3
2
1
r
1
2
ρ

The effect of the intensity of light was tested twice, once with a total volume of 30 c.c., and once with a total volume of 300 c.c. Two reaction vessels were arranged, one in bright sunlight and one in diffuse light, and the reactions in the two were allowed to proceed simultaneously. It will be observed that the ratio r is unaffected by light intensity in the large-volume runs. In the small-volume runs concentration effects play a part.

TABLE 5

Atmosphere	cm^3 Oxalate	cm^3 Bichloride	ρ	Oxalate consumed	r	light	
H_2	20	10	2	....	0.871	bright	Simultaneous
	20	10	2	....	0.724	diffuse	
	200	100	2	1.872	0.872	bright	"
	200	100	2	1.735	0.869	diffuse	

Another experiment was tried. Eosin is of the type of substances which accelerate the formation of calomel. Runs were made in the presence of eosin in hydrogen and oxygen. The figures are as follows:

TABLE 6

Atmosphere		Oxalate consumed	r	Eosin	
H_2	2	1.603	0.856	10^{-5}M	Simultaneous
	2	0.732	0.860	0	
O_2	2	1.610	3.25	10^{-5}M	
	2	0.729	3.28	0	

The eosin was at the concentration at which it is reported to be most effective,[6] namely, 10^{-5} molal. It will be noticed that the presence of the eosin has an accelerating effect on the reaction but no effect on the ratio r. Also the values of this ratio are substantially the same as those listed in Table 4 and are much higher in oxygen than in hydrogen.

The effect of temperature was tentatively examined. As the range was only five degrees and no very careful means were employed to obtain constant temperature, the results are not to be used in calculating temperature coefficients. A table giving the effect of temperature on the production of calomel may be found in Eder's Handbuch der Photographie. (*Loc. cit.*)

TABLE 7

Atmosphere	ρ	Oxalate consumed	r	Temp.
H_2	2	1.356	0.852	20°
O_2	2	1.364	3.20	
H_2	2	1.493	0.856	25°
O_2	2	1.514	3.30	

It is evident that a rise in temperature is accompanied by an acceleration of the reaction but that r is affected but little, if at all.

DISCUSSION

From the results tabulated above, it is immediately evident that the reaction does not follow the simple equation assigned to it by previous experimenters. That equation should give a ratio, $\frac{\text{oxalate consumed}}{\text{calomel produced}}$ equal to unity. Moreover, not only does the reaction not follow that equation, but it cannot follow any single simple equation, because the ratio is not constant. The most reasonable conclusion is that not *one* reaction is taking place but two. Both oxalates and mercuric chloride are known to be photosensitive, though not in a degree comparable with the substances present in the reacting mixture. It is reported [7] that bichloride of mercury undergoes a decomposition under the influence of ultra-violet radiation, and it is well known that oxalic acid solutions are unstable in direct sunlight. The probability, then, is great that there are present two decompositions connected by some as yet uncertain relation.

Examining the data in more detail, another point is strikingly evident. The series of runs determining the effect of concentration showed that doubling the amount of either constituent doubled the amount of that constituent which underwent decomposition. It is by no means unreasonable to suppose that, in the early stages, the process is a combination of two "unimolecular" decomposition; for example,

$$Hg\,Cl_2 = 1/2\,Hg_2Cl_2 + 1/2\,Cl_2 \qquad (I)$$

$$C_2O_4'' = 2CO_2 + 2O \qquad (II)$$

If this is the case, how are the two reactions connected, for connected they must be, since neither takes place so rapidly alone? There is the evidence of boiling point measurements [8] to show that a complex exists in a mercuric chloride ammonium oxalate mixture. This must be the connecting link. Both mercuric and mercurous oxalates decompose readily on exposure to light, and it is therefore plausible to assume that a mercuric chloride oxalate complex would be much more photosensitive than either mercuric chloride or ammonium oxalate alone. Let us adopt the hypothesis, then, that

there is formed in the reaction mixture a complex, and that this complex is photosensitive. This complex, being formed of an oxidizing and a reducing agent, must exist in a state of strain, a strain represented in all probability by an electron in a greatly distorted orbit.

What evidence is there to substantiate reactions (I) and (II)? Reaction (I) is known to take place, but the formation of free chlorine should undoubtedly be followed by oxidation of the oxalate, which is known to be oxidized by bromine water.[9] And yet this does not take place because, in hydrogen, the ratio indicates an excess of bichloride reduced over oxalate oxidized. It is probable that the greater part of the oxalate is bound up in the complex, and that the chlorine attacks the water molecules first, forming free oxygen and hydrochloric acid. The presence of free oxygen in the gas above the reacting mixture in a carbon dioxide run has been established. This shows that bichloride, made sensitive in some way by the presence of oxalate, has undergone a decomposition without the oxalate being transformed into carbon dioxide. As to reaction (II), the most prominent difficulty is accounting for the electrons. It might easily be done if the reaction were written

$$C_2O_4'' = CO + CO_3''.$$

But Eder [10] reports that pure carbonic acid is the gaseous product of the reaction. We will leave this point momentarily.

The experiments on the effect of the atmosphere brought out the fact that oxygen is the exception. The reaction proceeds with the same speed and gives the same ratio in vacuo as in hydrogen. It is known, as was mentioned in the introduction, that the action of carbon dioxide is the same as that of hydrogen as far as regards calomel formation. Let us leave the oxygen runs for the moment and examine those made under hydrogen. The most striking fact about them is that they are all below unity except those which, having been obtained from small-volume runs, arose from reactions which had proceeded nearly to completion. And it has been noticed in passing that concentration affects the ratio greatly. The initial ratios under hydrogen may then be stated to be < 1, varying from ca. 0.9 to 0.2. Such values indicate that more bichloride is being reduced than oxalate oxidized.

Furthermore, in oxygen the initial ratios are very much higher

than unity. This means that relatively more oxalate is being consumed. It is here only reasonable to suppose that the oxygen is able to attack the oxalate made sensitive by radiation and by complex formation. But in this connection we must notice the interesting fact that oxygen does not increase oxalate consumption. The amounts of oxalate consumed under hydrogen and oxygen under the same conditions are substantially the same. The solution is not to be looked for in a specific action of hydrogen, but in that of oxygen. The effect of the last-named gas is to decrease calomel production. In other words, the old idea that oxygen was a "negative catalyst" is erroneous, since it affects only one-half of the process. The complex previously assumed, is capable of decomposition according to the process

$$\text{complex} \rightarrow Hg_2Cl_2 + 2CO_2 \qquad \text{(IV)}$$

Such a reaction would yield the stoichiometric ratio, unity, between ammonium oxalate and calomel. In addition to this reaction we have also some such reaction as

$$\text{complex} + HgCl_2 = Hg_2Cl_2 + 1/2\ Cl_2 + \text{complex} \qquad \text{(V)}$$

Reaction (V) shows the possibility of a low ratio because it provides for the production of calomel without simultaneous oxidation of oxalate.

Now in the presence of oxygen we should expect

$$\text{complex} + 1/2\ O_2 = + CO_2 + CO_3'' + \text{mercuric complex} \quad \text{(VI)}$$

The mercuric complex liberated would immediately recombine with more C_2O_4'', thus sensitizing it and rendering it more liable to oxidation. That no more oxalate is decomposed in the presence of oxygen may be explained by the relatively slow velocity of activation of the complex. It is probable that the formation of the complex, being an ionic reaction, is rapid, and that the decomposition of the complex is also rapid. The measurable speed of the process as a whole is due to the fact that activation of the complex by radiation is not instantaneous.

In this connection may be cited the experiments with eosin. This substance acted as a simple accelerator, leaving the stoichiometry of the reaction unaltered. This might be brought about in two ways. First, the reactants might be adsorbed in equal amounts and

so the total concentration would be increased without affecting ρ. Or the fluorescent dye might be capable of concentrating the radiation to which the reaction is sensitive. That this last is the case is shown by an experiment in which it appeared that the reaction went many times faster in a mixture behind a screen of water than behind a screen of eosin solution of equal thickness.

In spite of Eder's evidence cited above to the effect that only pure carbonic acid is a product of the reaction, it is by no means impossible that some oxalate decomposes into carbon monoxide and carbon dioxide. The resulting ratio would then depend on the relative velocity of the two reactions. In the absence of definite evidence as to the actual velocities the only positive conclusion to be drawn is that in the first phase of the process the consumption of the two reactants is proportional to their concentrations as long as the total concentration is nearly constant. The equation connecting the amount transformed, x, with the time, t, is, for such a "unimolecular" reaction

$$\frac{dx}{dt} = k_1(a_1 - x_1) \qquad (2)$$

where a_1 is the initial quantity of the component 1. A similar equation holds for component 2. Integrating (2),

$$k_1 t = ln\, a_1 - ln\,(a_1 - x_1)$$

or

$$x_1 = a_1(1 - e^{-k_1 t}) \qquad (3)$$

Similarly

$$x_2 = a_2(1 - e^{-k_2 t}) \qquad (4)$$

Hence, dividing (3) by (4),

$$\frac{x_1}{x_2} = \frac{a_1}{a_2} \frac{1 - e^{-k_1 t})}{1 - e^{-k_2 t})} \qquad (5)$$

But x_1/x_2 is exactly the measured ratio, r, and a_1/a_2 is exactly the initial ratio of the constituents, ρ. So

$$r = \rho \frac{1 - e^{-k_1 t})}{1 - e^{-k_2 t})} \qquad (6)$$

The initial value of r, $(t = 0)$ is readily seen to be

$$r = \rho k_1/k_2$$

or

$$r \propto \rho \qquad (7)$$

This is, of course, in accord with what was found. Quadrupling the original ratio of constituents quadrupled the measured ratio.

It should by now be sufficiently evident that this work is only of an exploratory nature. We have shown definitely that the reaction, simple or accelerated, does not follow the simple equation given in the literature. We have also shown that, in its first stages, the process acts like a combination of two unimolecular reactions. We have shown that the intensity of the light has no effect on the ratio. But there remain many questions. What is the actual velocity of the two reactions? What are the orders of the reactions? What is the nature of the complex? What effect has the wave length of light on the ratio? To this last question we may make a qualitative answer. Since the experiments were carried out in sunlight which had passed through window glass the extreme ultra-violet may be eliminated. On the other hand, qualitative experiments with light filters show that the blue end of the spectrum has most effect on calomel formation.

SUMMARY

It has been shown that the reaction between mercuric chloride and ammonium oxalate does not follow the simple equation assigned to it by previous investigators:

$$2HgCl_2 + (NH_4)_2\,C_2O_4 = Hg_2Cl_2 + 2CO_2 + 2NH_4Cl.$$

An accurate method has been developed for studying the reaction.

It has been shown that the first stages of the reaction follow equations derived from assuming the existence of two simultaneous "unimolecular" reactions in which the concentration of the reactants is proportional to the amount decomposed.

It has been shown that the effect of oxygen is to decrease calomel formation without affecting oxalate decomposition.

It has been shown that hydrogen and nitrogen give the same results as experiments run in vacuo.

It has been shown that the presence of eosin accelerates the rate of reaction but does not affect the stoichiometry of the process.

A hypothesis has been developed to explain the facts.

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BIOGRAPHY

THOMAS HUGER HAZLEHURST, JR., was born at Corinth, Mississippi, on March 11, 1906. His education was secured in Charleston, S. C. He graduated from Porter Military Academy, a secondary school of that city, in 1919, and received the degree of bachelor of arts from the College of Charleston in 1923. His major subjects were Mathematics and English. He registered in the graduate department of Chemistry, The Johns Hopkins University, in 1923, holding a Hopkins Scholarship. This Scholarship was renewed in 1924. In 1926 he was graduate assistant in chemistry.